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Abstract: Ultrafast dynamics of molecules at solid-liquid interfaces are of outstanding importance in chemistry and physics due to their involvement in processes of heterogeneous catalysis. We present a new spectroscopic approach to resolve coherent, time-resolved, two-dimensional (2D) vibrational spectra as well as ultrafast vibrational relaxation dynamics of molecules adsorbed on metallic thin films in contact with liquids. The setup is based on the technique of Attenuated Total Reflectance (ATR) spectroscopy which is used at interfaces between materials that exhibit different refractive indices. As a sample molecule we consider carbon monoxide adsorbed in different binding configurations on different metals and resolve its femtosecond vibrational dynamics. It is presented that mid-infrared, multi-dimensional ATR spectroscopy allows for obtaining a surface-sensitive characterization of adsorbates' vibrational relaxation, spectral diffusion dynamics and simple inhomogeneity on the femtosecond timescale.

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Ultrafast, Multi-Dimensional Attenuated Total Reflectance Spectroscopy Of Adsorbates at Metal Surfaces

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ABSTRACT

Ultrafast dynamics of molecules at solid-liquid interfaces are of outstanding importance in chemistry and physics due to their involvement in processes of heterogeneous catalysis. We present a new spectroscopic approach to resolve coherent, time-resolved, two-dimensional (2D) vibrational spectra as well as ultrafast vibrational relaxation dynamics of molecules adsorbed on metallic thin films in contact with liquids. The setup is based on the technique of Attenuated Total Reflectance (ATR) spectroscopy which is used at interfaces between materials that exhibit different refractive indices. As a sample molecule we consider carbon monoxide adsorbed in different binding configurations on different metals and resolve its femtosecond vibrational dynamics. It is presented that mid-infrared, multi-dimensional ATR spectroscopy allows for obtaining a surface-sensitive characterization of adsorbates' vibrational relaxation, spectral diffusion dynamics and sample inhomogeneity on the femtosecond timescale.

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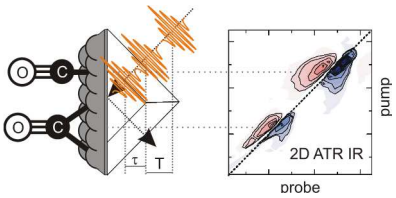


KEYWORDS

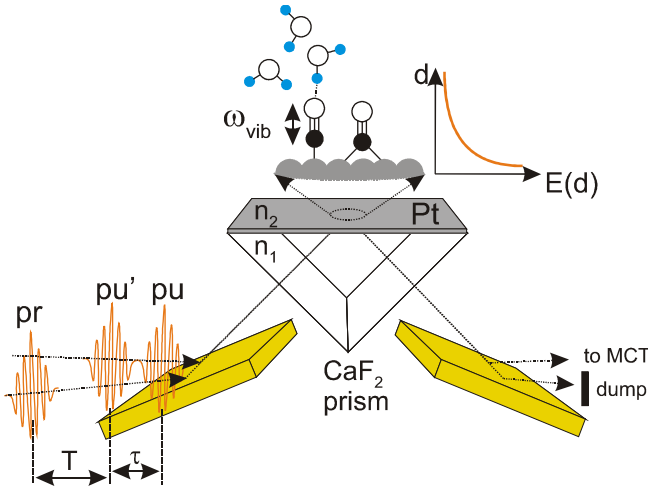
Coherent two-dimensional spectroscopy, attenuated total reflectance, vibrational dynamics, infrared, interfaces, adsorbates, carbon monoxide

Vibrational dynamics at interfaces are at the forefront of current interest in time-resolved spectroscopy.[1–5] In particular, vibrational spectra and dynamics on timescales of femto- to picoseconds for molecules adsorbed on solid substrates bear important information on processes such as photo-induced chemical reactions, interaction of samples with local environment and molecular structure. In this context, solid-liquid and solid-gas interfaces are important samples since they are involved in heterogeneous catalysis of chemical reactions.[6–8]

A versatile method for gaining vibrational and structural information about molecules at interfaces is Attenuated Total Reflectance (ATR) infrared (IR) spectroscopy.[9–11] Stationary ATR IR spectroscopy is widely applied to obtain linear vibrational spectra of a broad range of samples including self-assembled monolayers[12], heterogeneous catalyzed reactions[9] or bio-chemical systems[13]. It is thus astonishing that no attempts have been made as of yet to combine the ATR IR technique with established methods from ultrafast, multi-dimensional spectroscopy. Exactly this path is taken here by merging two extremely powerful methods of vibrational spectroscopy, *i.e.* ATR IR and femtosecond, pump probe and two-dimensional (2D) IR spectroscopy[14–16]. Using an ATR sample cell in a 2D IR spectrometer, it becomes possible to fully characterize vibrational dynamics and acquire multi-dimensional spectra of molecules at surfaces. With carbon monoxide (CO) adsorbed at different metal surfaces as a reference system, we report on pump probe and 2D ATR IR signals of molecules adsorbed from the liquid phase at different thin-film metal-water interfaces.

Our method uses a single-reflection ATR cell with a CaF_2 prism as a substrate (Scheme 1). Using CaF_2 as an ATR material avoids multi-photon IR absorption of pump pulses which occurs in alternative substrates such as ZnSe, Ge or Si. The ATR cell is combined with a 2D IR setup in pump probe configuration[17,18] (for details, see Experimental). Pump and probe beams enter the ATR prism with a mutual angle of ~7° and both with an angle of ~85° with respect to the normal of the ATR plane of the prism. This angle is chosen in order to

maximize reflectance signals that occur far away from the critical angle of the CaF_2/water system (~70°) used here. At the ATR interface, evanescent fields E(d) of pump and probe beams penetrate into the medium of lower refractive index ($n_2 < n_1$).[9] CO molecules adsorbed on, *e.g.* Platinum (Pt) or Gold/Palladium (Au/Pd) alloys within the penetration depth (d) can thus be addressed. Here we use very thin (< 1 nm) layers of metals sputtered on the ATR prism for two reasons. Firstly, IR excitation pulses can induce carrier dynamics in the only partially IR-transparent metal (*vide infra*). Reduction of the layer thickness reduces this effect and singles out the response of the adsorbate. Secondly, thick metal layers (>> 1 nm) can influence band-shapes of adsorbates in ATR experiments.[19] This effect plays a negligible role if sub-nanometer layers are used.



Scheme 1. Schematic ultrafast ATR experiment in pump-probe configuration for multi-dimensional dynamics of carbon monoxide (CO) adsorbed at a metal-liquid (*e.g.* Platinum (Pt)-water, grey) interface. Pulses pu and pu', separated by τ, are spatially overlapped on the reflecting plane of an ATR element with a pr pulse, delayed by population time T. Evanescent fields, E(d), penetrate into material of refractive index ($n_2 < n_1$).

At metal surfaces, CO can be either bound in linear or in bridged/multi-bound configurations (Scheme 1).[20] If CO-saturated water is flown above the Pt-coated ATR prism, in-situ

measured stationary ATR spectra show predominately one asymmetric band at ~2050 cm^{-1} in the investigated spectral region (1900 – 2100 cm^{-1}, blue, Fig. 1). In contrast, if a similar layer of Au/Pd is used, adsorbed CO shows two asymmetric bands at ~2045 cm^{-1} and 1930 cm^{-1} (red) which correspond to linear- and bridged/multi-bound CO, respectively.[20] The bands exhibit a width of about 30 – 40 cm^{-1}, typical for CO on thin metal-layers.[20]

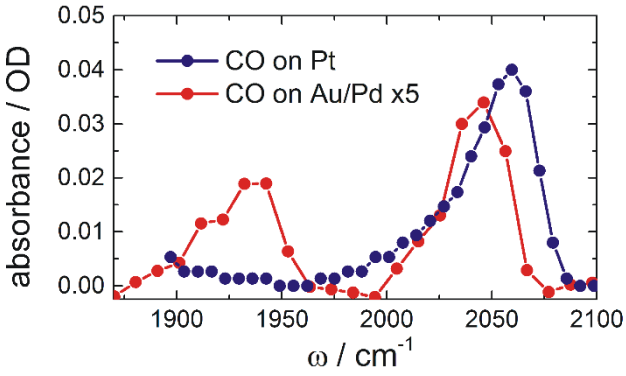


Figure 1. Stationary ATR infrared spectra of CO adsorbed on thin metal films. The blue spectrum represents CO adsorbed on Platinum (Pt). The red spectrum represents CO adsorbed on Gold/Palladium (Au/Pd, (80/20)). ω represents the vibrational frequency.

Excitation of adsorbed CO with ~100 fs IR pulses results in vibrational relaxation on femto- to picosecond timescales (Fig. 2). For CO on Pt, a combined ground state bleach/stimulated emission (GSB/SE) band is observed at ~2050 cm^{-1} (~30 – 40 cm^{-1} FWHM) together with a broad (> 50 cm^{-1} FWHM) excited state absorption (ESA) band. The ESA signal is initially (≤ 300 fs) centered around 1975 cm^{-1} and blue-shift to ~2010 cm^{-1} within picoseconds while the GSB/SE signals blue-shift on the same timescale, but with moderate spectral changes (~ 10 cm^{-1}). ESA and GSB/SE signals of CO decay within ~20 ps leaving behind a broad enhanced reflectance signal that slowly decays on a timescale of hundreds of picoseconds. This slowly decaying signal originates from a photo-excitation process of the metal electrons near the Fermi-edge: starting from a non-equilibrium electron distribution directly after mid-

IR excitation, energy redistribution predominately to lattice phonons of the metal, or surrounding molecules (*e.g.* solvent) quickly (<< 1 ps) establishes a hot electron distribution near the Fermi-edge as well as a vibrationally-excited lattice.[3,21] Both of these contributions subsequently cool down again on timescales of multiple tens to hundreds of picoseconds, depending on the employed experimental conditions. Details about the observed dynamics will be presented elsewhere. Fitting of the pump probe data (Fig. 2 (c), blue symbols) with a double exponential function (black line) reveals time constants for the CO- and metal-related signals as 3.6 ps and > 400 ps, respectively.

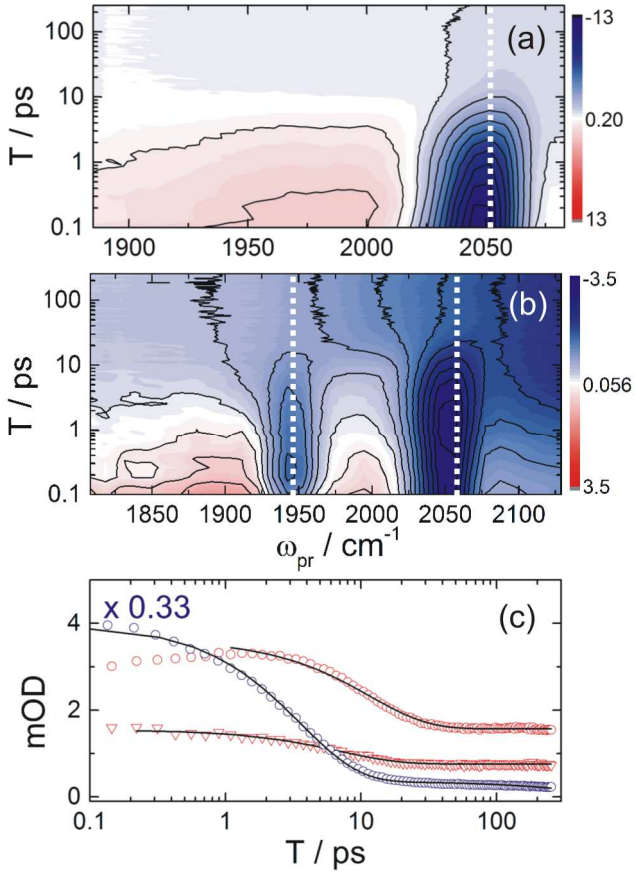


Figure 2. ATR pump probe signals of CO on (a) Pt and (b) Au/Pd. Blue and red signals represent GSB/SE and ESA, respectively. The colored axis is in mOD and ω_{pr} represents the detection frequency. (c) Representative cuts at positions indicated with dashed lines in (a) and (b) for Pt (blue) and Au/Pd data (red, circles: ~2050 cm^{-1}; triangles: ~1950 cm^{-1}). Solid lines represent bi-exponential fits.

Analogous signals from CO adsorbed on Au/Pd (80/20) reveal the CO dynamics for different binding configuration (Fig. 2 (b)). GSB/SE and ESA signals are observed for bridged and linear CO at 1940 cm^{-1}/2050 cm^{-1} and 1900 cm^{-1}/1980 cm^{-1}, respectively. These again decay within about 20 ps. The bridged CO bands, however, decay slightly faster compared to the linear CO (*vide infra*). Only mild evolution of band positions (< 10 cm^{-1}) is observed compared to Pt data. Notably, the ESA signal of linear CO strongly overlaps with the GSB signals of the bridged CO, thus resulting in a pronounced difference in GSB signal intensities for the different binding configurations. Also in case of CO adsorbed on Au/Pd, a very slowly decaying enhanced reflectance spectrum is observed for hundreds of picoseconds after excitation. Again, this signal stems from excitation of the metal layer. The kinetic traces at GSB positions for CO on Au/Pd (red symbols, Fig. 2 (c)) are reasonably fit by a bi-exponential function with a very slow (>500 ps) and a ~9 ps component (~2050 cm^{-1})/ ~7 ps component (~1950 cm^{-1}). From these the former accounts for the decay of the metal-related signal while the later describes the CO-related dynamics.

While the above presented ATR pump probe experiments clearly allows for a characterization of vibrational relaxation, the obtained signals fail to reveal information such as disentanglement of strongly overlapping ESA and GSB/SE bands, quantification of inhomogeneous broadening or characterization of spectral diffusion. This information can be obtained from absorptive ATR 2D IR signals at different population times. For instance, Fig. 3 shows characteristic 2D IR spectra for CO on Pt ((a) – (c)) and Au/Pd ((d) – (f)). The spectra have been obtained after subtraction of consecutively obtained datasets acquired for aqueous solutions with and without CO. Early 2D spectra (0 ps) for both samples exhibit ESA (red) and GSB/SE (blue) signals, strongly elongated along the diagonal (dashed line) for linear (Pt and Au/Pd) as well as bridged CO signals (only Au/Pd). This diagonal elongation

indicates a very inhomogeneous distribution of transition frequencies. On the other hand, the anti-diagonal width of ESA and GSB/SE bands is only low (~17 cm^{-1} for Pt, ~15 cm^{-1} for Au/Pd) compared to the diagonal width (35 – 40 cm^{-1}). From these values we can estimate a homogeneous dephasing time of ~0.3 – 0.35 ps.

The obtained 2D IR spectra moreover give an explanation of shapes and spectral evolution of the congested pump probe spectra (Fig. 2). Consider for instance CO on Pt which shows initially strongly separated ESA and GSB/SE signals (Fig. 2 (a)). At 0 ps, the 2D spectrum (Fig. 3 (a)) shows elongated GSB/SE and a similarly influenced ESA signal (~2020 cm^{-1}). Projection of the 2D spectrum onto the probe axis results in partial cancellation at the blue-detuned wing of this ESA signal which shifts of the ESA maximum to lower frequencies. As relaxation proceeds, this cancellation of ESA and GSB/SE signals is diminished due to the rotation of ESA and GSB/SE bands.

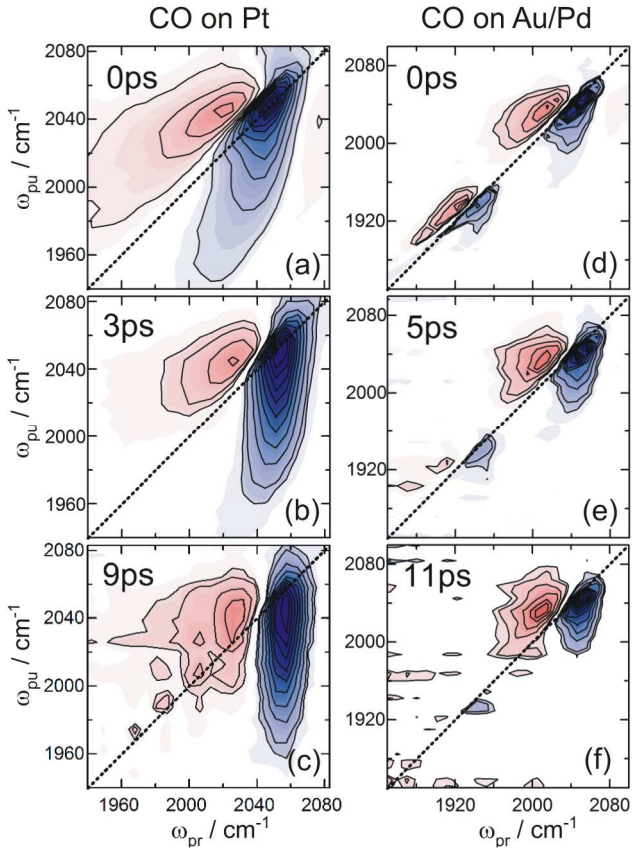


Figure 3. ATR 2D IR signals of CO on Pt ((a), (b), (c)) and Au/Pd ((d), (e), (f)) in dependence of population time T. Blue signals represent to GSB/SE, red signals represent to ESA. Contour lines are drawn equally spaced at 10% increments. $\omega_{pu/pr}$ represent the excitation and detection frequency, respectively.

Additionally, the 2D spectra also reveal more detailed information about vibrational anharmonicities. Still, exact values can only be obtained from fitting 2D spectra to a model including a realistic lineshape function.[14] Differences of maxima and minima obtained from 2D spectra of CO on Pt consistently give values of about 25 cm^{-1}. This value is thus larger as generally observed for, *e.g.* transition metal-carbonyl complexes[22,23] but similar as for gas-phase CO.[24] 2D spectra of Au/Pd data furthermore allow one to compare anharmonicities for linear and bridged CO. Here, linear CO obtains an even larger shift of about 30 cm^{-1} while bridged CO shows values of only 15 – 20 cm^{-1}. From these values it can be estimated that the potential curve of bridged CO is more harmonic compared to linear CO.

Finally, 2D IR spectra at various population times report on spectral diffusion as local sample environments interconvert.[14] A measure for spectral diffusion is represented by the temporal changes of the nodal slope between ESA and GSB/SE signals in 2D IR spectra (Fig. 4).[14] Applying single exponential fits together with static offsets to the data, we find time constants for spectral diffusion for CO on Pt and Au/Pd as 6.0 ps and 6.4 ps, respectively. A likely origin of inhomogeneity is represented by local dynamic solvation of CO molecules after excitation. The similar time constants observed for Pt and Au/Pd data suggest that solvent interaction, possibly via hydrogen-bonding with water, is the dominant source of this term.

A second feature in the spectral diffusion data is the appearance of different static offsets which are required to fit the data to a single exponential decay. In case of Au/Pd a significant offset of 0.47 is observed while for Pt data the offset is only very low ~0.01. An additional

source of inhomogeneity is represented by static structural heterogeneity of the metal layer which could explain the significant offset in case of Au/Pd data. In this regard, different static inhomogeneity can be expected since sputtered alloys of Au/Pd should obtain more spatially-varying environments compared to layers consisting of pure Pt. The significantly lower static offset observed for Pt data is, however, astonishing in the sense that sample inhomogeneity for the sputtered Pt layer would originate predominately from local solvation whereas local static structures play only a minor role. In fact, very thin (< 1 nm) layers of Pt are expected to exhibit non-uniform sample properties such as thickness and morphology[25], possibly including formation of metal islands on the substrate from which a larger static contribution would be expected. A consistent reasoning of the missing significant static offset in the spectral diffusion data for Pt thus requires further investigation by use of CO adsorption on, *e.g.* single crystal surfaces of different metals as well as sputtered surfaces from a broad range of preparation conditions. The results of such experiments will be reported elsewhere.

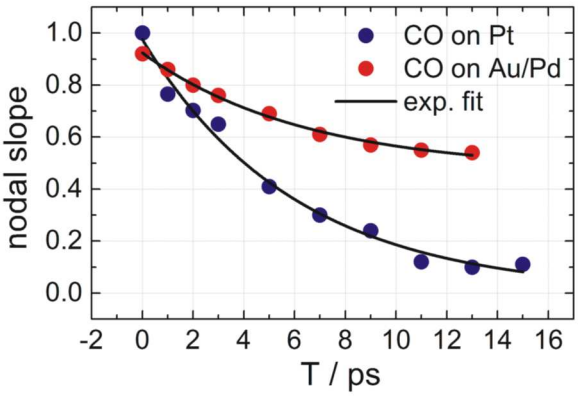


Figure 4. Spectral diffusion dynamics of linearly adsorbed CO. Symbols represent experimental data for CO on Pt (blue) and CO on Au/Pd (red). Solid lines represent exponential fits.

The above presented results highlight the capabilities of ultrafast, multi-dimensional ATR spectroscopy for studying vibrational dynamics of molecules at metal-liquid interfaces. Surface-adsorbed CO has been investigated previously with numerous techniques, including FT-IR ATR spectroscopy.[19,26,27] Our data correspond well to these previous reports in terms of asymmetric band shapes, positions or intensities. With regard to ultrafast measurements, vibrational relaxation of adsorbed CO has also been investigated by use of different methods and yielded time constants that lie in a rather broad range of 2 - 8 ps.[1,24,28–30] Taking into account different preparation conditions, influence of employed metals and experimental temporal resolution, literature values correspond reasonably with the dynamics encountered here (3 – 10 ps). A reasoning for the different lifetimes derived here for CO on sputtered metal layers and previous values is most likely that reported short lifetime values have been observed mainly for samples at single crystal surface.[2,24,28,30]

To the best of our knowledge, only a single work investigated multi-dimensional signals of adsorbed CO by use of heterodyne-detected Sum-Frequency-Generation (SFG) spectroscopy.[31] Although different preparation conditions for metal surfaces and sample solutions were used in these experiments, values for, *e.g.* anharmonicities from 2D spectra are similar (22 cm^{-1})[31] as derived here and sample inhomogeneity has been pointed out as well. However, no characterization of vibrational dynamics were reported. Here, we unraveled such dynamics using 2D IR ATR signals which report on spectral diffusion and quantification of static inhomogeneity as well as vibrational relaxation dynamics for linear and bridged CO.

One certainly powerful advantage of 2D IR spectroscopy is the possible resolution of vibrational coupling or energy transfer by identification of cross-peaks between bands in the 2D IR spectra.[14] Regarding results on surface absorbed CO, cross-peaks may be thought to appear between linear and bridged bound CO molecules or between subsets of oscillators within the asymmetrically broadened band for linear CO. From the current data (Fig. 3), such

features can, however, not be identified unambiguously, allowing for the conclusion that, *e.g.* interaction between different CO binding configurations is very low or even negligible.

In the context of spectral, temporal and structural information of molecules at interfaces, femtosecond SFG spectroscopy is the most commonly used approach for obtaining such information.[1,2,4,31] In contrast to ATR spectroscopy, SFG exploits combinations of IR and visible laser pulses to derive vibrational spectra of molecules in exclusively non-centro-symmetric environments. SFG has even earlier been demonstrated to yield phase-sensitive 2D IR spectra and dynamics.[2,31] However, especially when high temporal resolution and phase-sensitive, multi-dimensional information is sought, SFG spectroscopy is experimentally more demanding compared to ATR. This is due to the fact that SFG involves creation of multiple beams with different frequencies and phase-stability in the visible.[31] On the other hand, SFG has the great benefit not to be restricted to interfaces involving solids which allows a broader range of samples to be studied.

In conclusion, we have presented a versatile approach for resolving multi-dimensional, ultrafast, vibrational dynamics of molecules adsorbed at interfaces by Attenuated Total Reflectance spectroscopy. Specifically, we have measured pump probe and 2D IR spectra of linear- and bridged-bound CO on Platinum and Gold/Palladium thin layers adsorbed from aqueous solutions. A broad range of aspects of vibrational dynamics have been characterized in detail including vibrational relaxation, spectral diffusion, as well as information concerning congested transient spectra, anharmonicity and static sample inhomogeneity. The results demonstrate that a 2D IR experiment can be straightforwardly upgraded for studying ultrafast dynamics with surface-sensitivity. 2D ATR IR spectroscopy thus has the potential to result in a broad range of applications for ultrafast, interface-related research.

EXPERIMENTAL

Infrared beams are generated from a single optical parametric amplifier (OPA)[32] giving ~1.5 µJ pulse energy at 5 kHz. A fraction (~100 nJ) of the OPA output is taken with a BaF_2 wedge as probe and reference beams (pr/ref) for balanced detection. For 2D IR experiments, a Mach-Zehnder interferometer is introduced to the pump beam, delivering replica of pump pulses (pu/pu') as described elsewhere[18]. ATR prisms (10 x 10 mm, CaF_2) are sputter-coated with metal films (< 1 nm) whose thickness is determined with a quartz-microbalance. Pu/pu' and pr/ref beams are focused on the back side of the reflecting plane of the prism using off-axis concave (r = 30 cm) and plane gold mirrors. After recollimation, pr/ref pulses are detected by a 2x32pixel MCT array.

Doubly de-ionized water is saturated with Argon (4.8 Pangas) followed by CO (4.8 Pangas). The solution is slowly flown at the metal-coated surface of the CaF_2 prism. CO adsorption is monitored by recording in-situ, stationary ATR spectra. Adsorption is complete within a few minutes and is constant during experiments, indicating good stability of the metal layer for at least 3 - 4 h.

Acknowledgements

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